#### Research Division

### NATIONAL RESEARCH CORPORATION 70 Memorial Drive Cambridge 42, Massachusetts

JPL Contract No. 950393
Contract No. NAS 7-100

NRC Project No. 44-1-0239

STUDY OF SUPERCONDUCTING

THIN FILMS	
<b>by</b>	GPO PRICE \$
Peter Fowler	OTS PRICE(S) \$
**************************************	Hard copy (HC)
Final Report	Microfiche (MF)

Approved by:

Philip J Clough, Assistant Director of Research

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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

Submitted to:

Jet Propulsion abboratory 4800 Oak Groye Brive Pasadena, California

3	N65 17508	
	(ACCESSION NUMBER)	(THRU)
FOR	35	
5	(PAGES)	(CODE)
PAGILITY	CR160873	20
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

# TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	iii
LIST OF TABLES	iv
INTRODUCTION	1
EXPERIMENTAL	2
Evaporation of Niobium	3
Evaporation of Tin	9 *
Measurement of Critical Current	10
Measurement of Thickness	12
Determination of Compound Formation	16
RESULTS	16
SUMMARY	30
ACKNOWLEDGEMENTS	31
REFERENCES	32

# LIST OF ILLUSTRATIONS

			Page
Figure	1	SCHEMATIC OF VACUUM EVAPORATION - CONDENSATION SYSTEM	5
Figure	1 <b>A</b>	VACUUM EVAPORATION - CONDENSATION SYSTEM	6
Figure	2	SUPERCONDUCTIVE - NORMAL TRANSITION FOR NIOBIUM FILM NO. 27B IN 25 KOE MAGNETIC FIELD	11
Figure	<b>3</b> , ,,,,,,,	13 KILO-OERSTED HORSESHOE MAGNET ASSEMBLY	13
Figure	4	30 KILO-OERSTED SOLENOID MAGNET ASSEMBLY AND HELIUM DEWAR	14
Figure	5	CRITICAL CURRENT VS. TRANSVERSE MAGNET FIELD FOR NIOBIUM FILMS	18
Figure	6	CRITICAL CURRENT VS. MAGNETIC FIELD FOR ~6000 Å NIOBIUM FILM NO. 7 ON CRYSTAL QUARTZ	19
Figure	7	CRITICAL CURRENT VS. MAGNETIC FIELD FOR ~5000 Å NIOBIUM FILM NO. 10 ON CRYSTAL QUARTZ	20
Figure	8	CRITICAL CURRENT VS. MAGNETIC FIELD FOR 800 Å NIOBIUM FILM NO. 27 ON CRYSTAL QUARTZ	21
Figure	9	CRITICAL CURRENT VS. MAGNETIC FIELD FOR Nb3Sn FILM NO. 36G	28

### LIST OF TABLES

			Page
Table	I	IMPURITIES IN NIOBIUM GRAVEL	4
Table	II	SUMMARY OF Nb3Sn EXPERIMENTS	25

#### INTRODUCTION

The purpose of the work reported here is to investigate the process of forming on cylindrical substrates superconducting thin film coatings of  $Nb_3Sn$  capable of conducting a current of  $10^5$  amperes per centimeter of cylinder length in a magnetic field of  $10^5$  oersteds or greater.

The work of necessity had to follow an exploratory course since no coatings with such properties are known to have been produced. In addition, a search of the literature found no report of the successful production of any hard superconductor using vacuum evaporation techniques except for limited success in preparation of tantalum films in ultra-high vacuum. Dr. Alvin F. Hildebrandt of Jet Propulsion Laboratory at the start of this program advised that we put our first effort into formation of niobium films by vacuum evaporation onto insulating and metallic substrates. The purpose of this would be to show our capability in producing superconducting niobium films before attempting the more difficult process of forming Nb<sub>3</sub>Sn films.

That capability was demonstrated by forming superconducting niobium films on crystal quartz, copper, and niobium substrates. The effort was then turned to formation of Nb<sub>3</sub>Sn by vapor reaction techniques.

Both sequential and simultaneous deposition of Nb and Sn vapors was carried out onto substrates which were heated in various manners in order to bring about reaction to form Nb<sub>2</sub>Sn.

Testing of the conductive properties of all films produced was done in external magnetic fields up to 30,000 oersteds.

While progress was made on the proposed program, the investigation was continued on a self-sponsored basis by National Research Corporation with the result that two small films of Nb<sub>3</sub>Sn as identified by X-ray diffraction were produced. The process variables were investigated and some progress was made in defining the conditions necessary for consistently forming Nb<sub>3</sub>Sn coatings.

#### EXPERIMENTAL

Niobium and tin were evaporated from separate sources. The rate of evaporation of each source was determined by measurement of the increase in weight of a glass microscope slide and by measurement of the resistance of the deposit on the substrate.

Substrates of niobium, copper and crystal quartz were used.

All were .06 inches wide, 1 inch long, and no thicker than .025 inch.

The quartz was polished optically flat on the side to receive the film. The copper was mechanically and electrolytically polished.

The niobium ribbon had a mill finish. All substrates were treated in boiling detergent, rinsed with distilled water and dried in a clean oven just prior to being placed in the vacuum chamber. Prior to deposition of the coatings the samples were heated by radiation from a niobium ribbon to temperature higher than they would experience

during deposition. This was to insure that excessive outgassing of the surface not occur during deposition.

The source to substrate distance is 13 cm. We desire that a 2 cm length of the substrate have a uniform film. From Holland we find that the thickness obtained at a point 1 cm from the zenith of a source 13 cm below is 99% of the thickness obtained at the zenith. Thus our films would be uniformly thick to within the order of 1%.

The vacuum system is pumped by an NRC 750 liters per second HS-4 diffusion pump. A liquid nitrogen filled trap is in the pumping line to the chamber and the chamber is water cooled when evacuated and is heated with hot water when open to the atmosphere and during the evacuation process in order to encourage the proper outgassing of the chamber.

# A. Evaporation Of Niobium

The evaporation of niobium was carried out using electron bombardment of 99.6% pure niobium gravel. An analysis of the gravel is given in Table I. Gravel was used since it was readily available in high purity and due to the ease with which one may replenish the crucible.

Figure 1 is a schematic of and figure 1A is a picture of the electron bombardment system and the associated vacuum facilities. The accelerating voltage used is 20 kilovolts. By controlling the temperature of the cathode the beam current may be varied up to 3 amperes

IADLE I

# IMPURITIES IN NIOBIUM GRAVEL

ELEMENT	AMOUNT	PRESENT	(PERCENT)	
С		0.02		
0		0.15		
<b>N</b>		0.047		
<b>Ti</b>		Not Det	tectable	
Fe		0.03		
Ni		0.005		
<b>A1</b>	•	0.03		
Со		0.005		
Cr		0.02		
<b>C</b> u		0.008		
Мо		0.01		
Ta		Probab:	le 0.15	

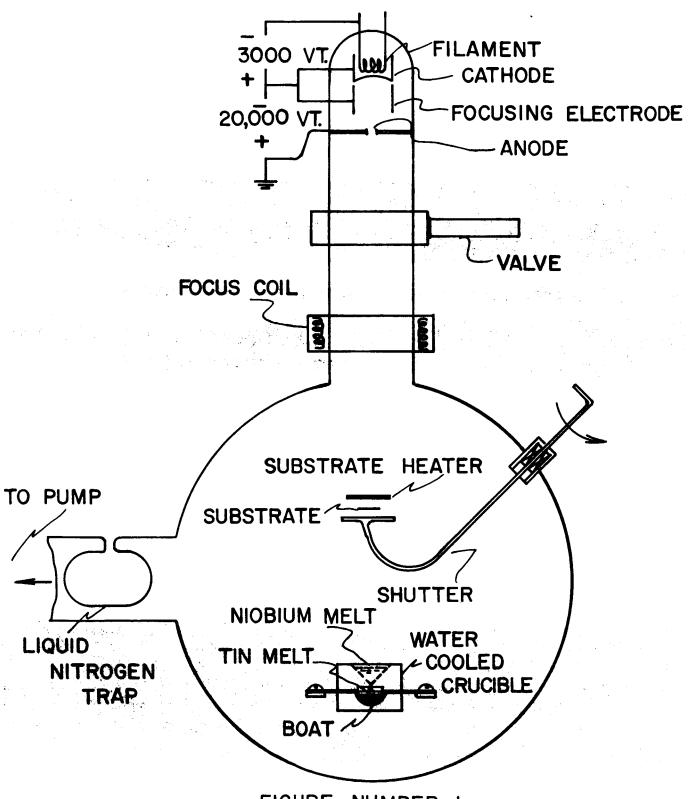
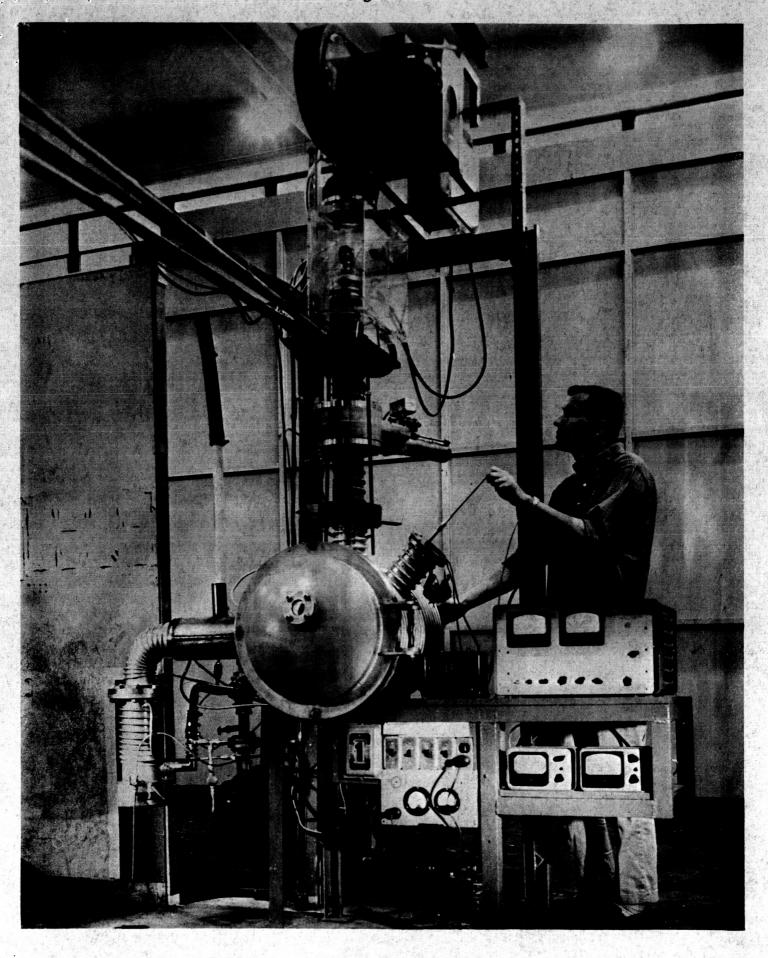


FIGURE NUMBER I SCHEMATIC OF VACUUM EVAPORATION CONDENSATION CHAMBER



thus giving us a capability of attaining 60 kilowatts of power input to the niobium. The evaporations carried out during this investigation were at 11 to 13 kilowatts input. Higher powers than this would cause evaporation rates higher than desired for the proper control of film thickness. The above power levels yielded condensation rates in the order of 400 Angstroms per second to 1200 Angstroms per second on a substrate 13 cm distant. The thickness of deposit condensed per second from a surface source of area A at distance h large compared with the size of source or receiver is given, approximately, by Holland 2 as,

$$= \frac{\sqrt{A}}{\sqrt{A}} (cm/sec)$$

where,  $\sigma$  = rate of evaporation per unit area of material from A, c = density of evaporant,

and h = source-substrate distance.

Thus we may calculate the rate of evaporation of niobium from our crucible. The area A is not known well since the beam strikes the middle of the melt and from here to the crucible wall the temperature drops off. The diameter of the melt is 3 cm.

We shall assume the area A from which the evaporation takes place is of radius 1 cm. The density of niobium is = 8.55 g/cm<sup>3</sup> and thus from the above relation we find that

$$\sigma = \frac{\pi (k^2 t)}{A} = 1.45 \times 10^{-5} \text{ t (Å/second)}$$

Therefore, the condensation rates noted above are found to correspond to evaporation rates of  $5.8 \times 10^{-3} \text{ gm/cm}^2$  second to  $1.74 \times 10^{-2} \text{ gm/cm}^2$  second. The data of Honig<sup>3</sup> and use of Langmuir's<sup>4</sup> formula shows that these rates of evaporation correspond, approximately, to temperatures of the melt of from  $3100^{\circ}$  C to  $3250^{\circ}$  C and to vapor pressures of from 0.6 torr to 2 torr, respectively.

Because of these very high evaporation rates the purity of the condensed deposit should be relatively uneffected by the residual gases present in the vacuum system. The purity of the deposit will also be increased over that of the starting material due to the very high temperature vacuum melting of the niobium which is carried out before each deposition of material. It is seen from Honig<sup>3</sup> that all elements present have a higher vapor pressure than niobium except tantalum. Between the vapor source and the substrate is interposed a shutter which effectively shields the substrate from the volatile constituents during this vacuum melting. The vapor pressure of tantalum is about 1/40 that of niobium so that one finds (ref.2, p.185) that there should be less than 0.005% tantalum impurity in the films.

The heat generated in the bombardment causes outgassing of the chamber surfaces. However, as the evaporation of niobium proceeds a coating of niobium is deposited on these surfaces which leads to decreased outgassing. The result of these competing

effects is that the chamber which had a capability of attaining a vacuum of  $10^{-7}$  torr is maintained at a higher pressure than this during evaporation. Initial outgassing causes the pressure to rise to  $10^{-4}$  torr but it soon drops to the  $10^{-6}$  torr range. This vacuum is more than sufficient for maintaining a steady controlled electron beam current and thence a steady evaporation rate.

# B. Evaporation Of Tin

Both direct and indirect heating of tin was carried out.

The indirect method consisted of putting the tin in a BN or Al<sub>2</sub>0<sub>3</sub> crucible surrounded by resistively heated tantalum or molybdenum foil. In addition there were 2 concentric heat shields of tantalum or molybdenum. It was found that to attain the 1400°C to 1550°C which is necessary for the required vapor pressure of tin, the heater strip must be run at temperatures which lead to its rapid deterioration especially in the presence of tin vapor.

Thus, the use of electron bombardment of the crucible in conjunction with radiant heating was investigated in the possibility that lower heater temperatures might be used. The crucible was flame sprayed with molybdenum to act as the anode. An electron power input to the crucible of over 100 watts was attained but the presence of tin vapor and outgassing led to a discharge and electrical breakdowns which made control of the evaporation difficult.

Direct heating of tin in a resistively heated boat of molybdenum or tantalum was found to be more successful. However, if the boat contained two little tin, the power input from the constant voltage supply varied with time due to the decreasing conductance of the boat. This situation was improved by using a large reservoir boat with a slotted cover of graphite added in order that the vapor issue as slowly as possible so that the conductance of the boat might remain effectively constant during an evaporation run.

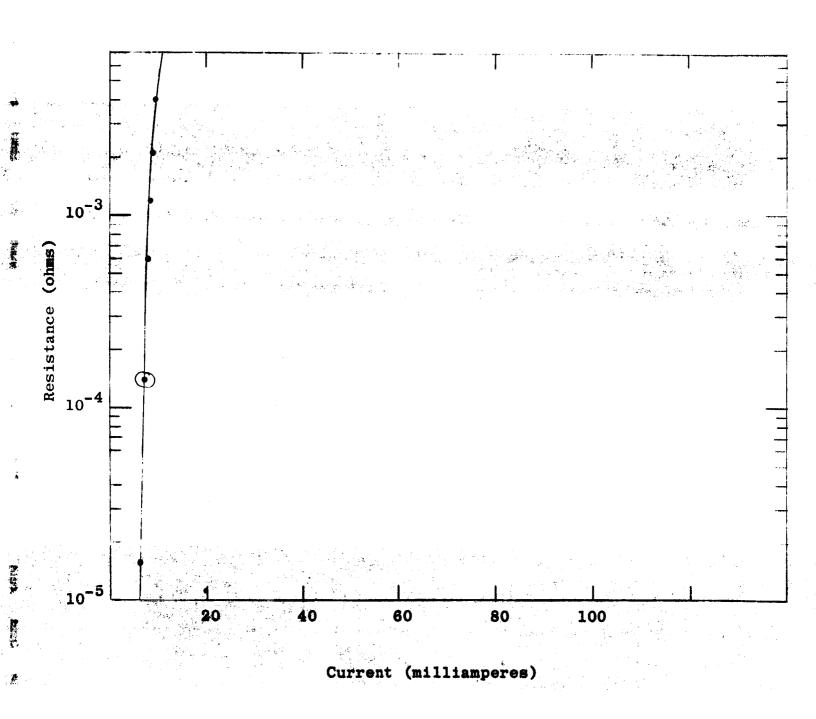
# C. Measurement Of Critical Current

According to common practice the critical current is taken as that current which causes a given voltage drop along the sample. We have chosen that voltage drop to be one microvolt along our 1 inch long .06 inch wide samples. For the sample currents and thicknesses we measure this corresponds to a maximum sample resistivity of approximately 10<sup>-8</sup> ohm-cm and a minimum of 10<sup>-12</sup> ohm-cm which is much less than the residual resistivity of the sample. Figure 2 displays a plot of the superconductive to normal state transition for an 800 Angstrom thick niobium film. The circled point corresponds to 1 microvolt potential drop and is taken to define the critical current. It is seen that the transition is quite abrupt and thus use of the one microvolt criterion is justified.

Measurement of the critical current is carried out by immersing

Figure 2

# SUPERCONDUCTIVE-NORMAL TRANSITION FOR NIOBIUM FILM #27 B IN 25 KOE MAGNETIC FIELD

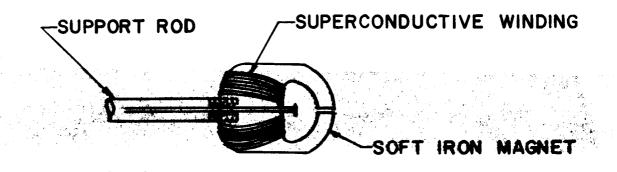


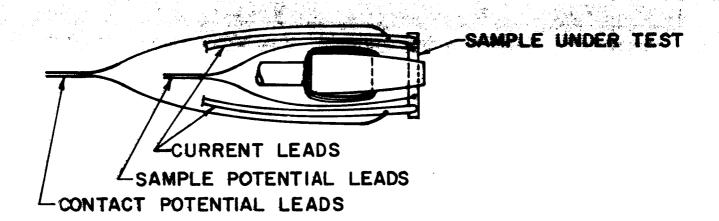
the sample in liquid helium and generating a magnetic field around the sample. Figure 3 and 4 show, respectively, the horseshoe and solenoid magnets for generating transverse and longitudinal magnetic fields. The diagram of the horseshoe magnet also shows the method of mounting a sample in the gap and the electrical connections made. The current is passed through 1/8 inch copper tubing to the sample. Contact from the copper tubing to the sample is made with 50% (by weight) indium, 50% tin solder. The sample is prepared for soldering by first applying the solder with an heated ultrasonic soldering iron (Sonabond Model S-O-HN-56-4).

Potential leads are soldered to the sample and to the copper leads as indicated in Figure 3. With these leads the potential drop of the sample and the sample plus contacts, respectively, are measured with Keithley 204A electronic galvanometers. The former potential drop is used to define the superconducting to normal state transition and the latter to monitor the power dissipation at the contacts with its consequent effect on the temperature of the sample. The sample current is controlled by a variable resistance in series with the sample and a 6 volt lead storage battery.

# D. Measurement Of Thickness

Measurement of the thickness of films thicker than 0.1 mil was accomplished with a micrometer. For thinner films an approximate thickness, t, is determined by measuring the change in weight, △ M, of a microscope slide upon dissolving the film





# FIGURE NUMBER- 3 13 KILO-OERSTED HORSESHOE MAGNET ASSEMBLY

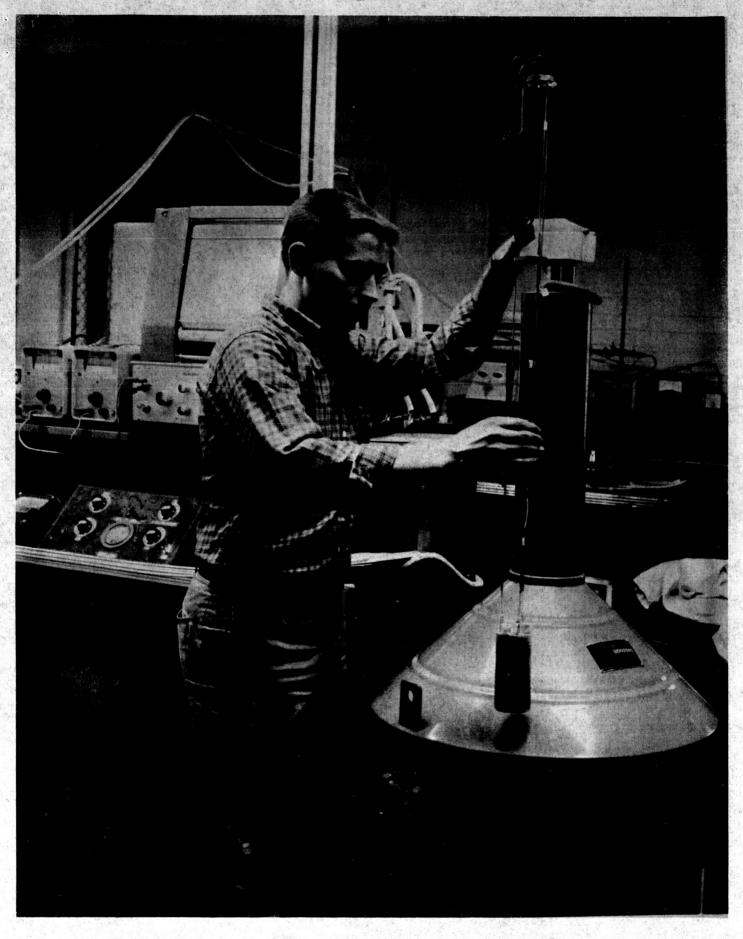


Figure 4:

from the substrate. Then:

where J = density of film

and A = area of the film.

The solvent is a solution of 30 g. ammonium bisulphate in 100 cc of sulphuric acid. This thickness determination suffers from the fact that a large area of film is required to attain sufficient mass for accurate weight measurement. Because the vapor source is relatively close to the slide the thickness varies along the slide and that calculated will be smaller than the thickness of the film on the relatively small sample substrate.

Another approximate determination of thickness is obtained from the room temperature resistance, R, of the film if we assume the bulk resistivity for the film to be that found in the various handbooks.

Then 
$$t = \frac{1}{R} \frac{R}{W}$$

where,  $\rho$  = room temperature resistivity of the film,

1 = length of film,

and w = width of film.

Since the lattice is probably strained therefore the resistivity
will be greater than the handbook value. This error would tend
to make the calculated thickness smaller than the actual thickness.

### E. Determination Of Compound Formation

In the case of niobium evaporation and no heat treatment, the resulting films were assumed to be pure niobium. In the case of evaporation of tin with niobium or when heat treatment of the films was made X-ray diffraction evidence was obtained using a Dubye-Scherrer camera to aid in identification of the compound.

Supplementary evidence of compound formation was obtained using the anodization techniques developed by Picklesimer 6 for the Nb-Sn system. The samples were anodized using 30 volts DC in the solution described in his paper.

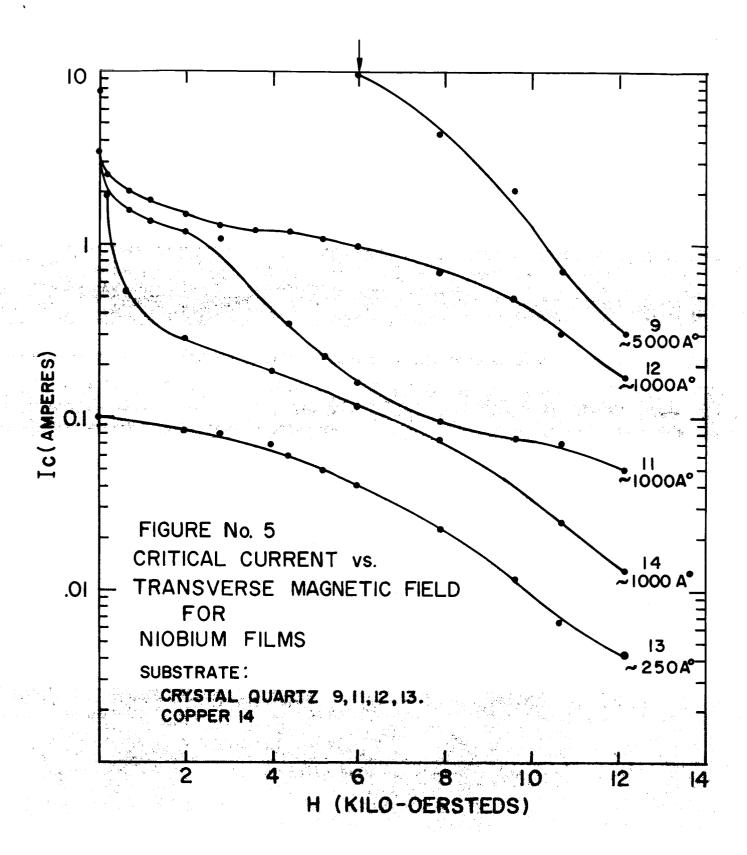
## RESULTS

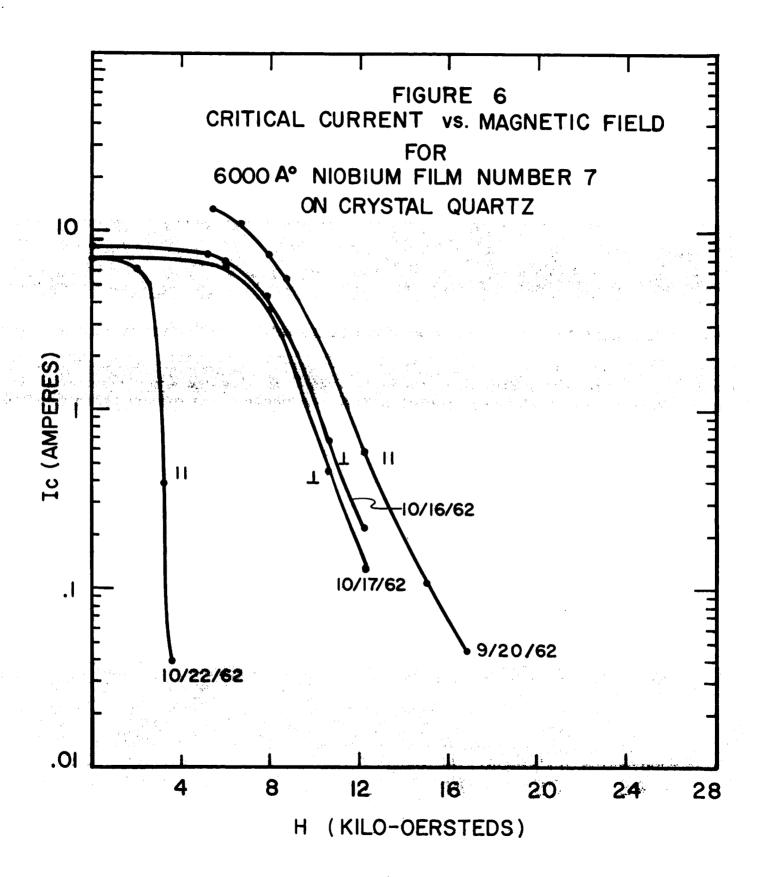
Since no report of superconducting niobium films formed by vacuum evaporation techniques has been found in the literature it was felt necessary that we develop fully the ability to form superconducting niobium films of varying thicknesses on substrates of both insulators and metals. Using 11 to 13 KW power input and preheating the substrates to 400°C a series of niobium films were formed on various substrates by opening a shutter (see Figure 1) for various predetermined lengths of time. During deposition of the film the substrate heater was set to maintain the substrate temperature at approximately 200°C as measured by a thermocouple attached to the substrate holder. However, due to the radiation from the niobium source and the heat of condensation of the niobium vapor the substrate holder temperature sometimes rose as high as 250°C.

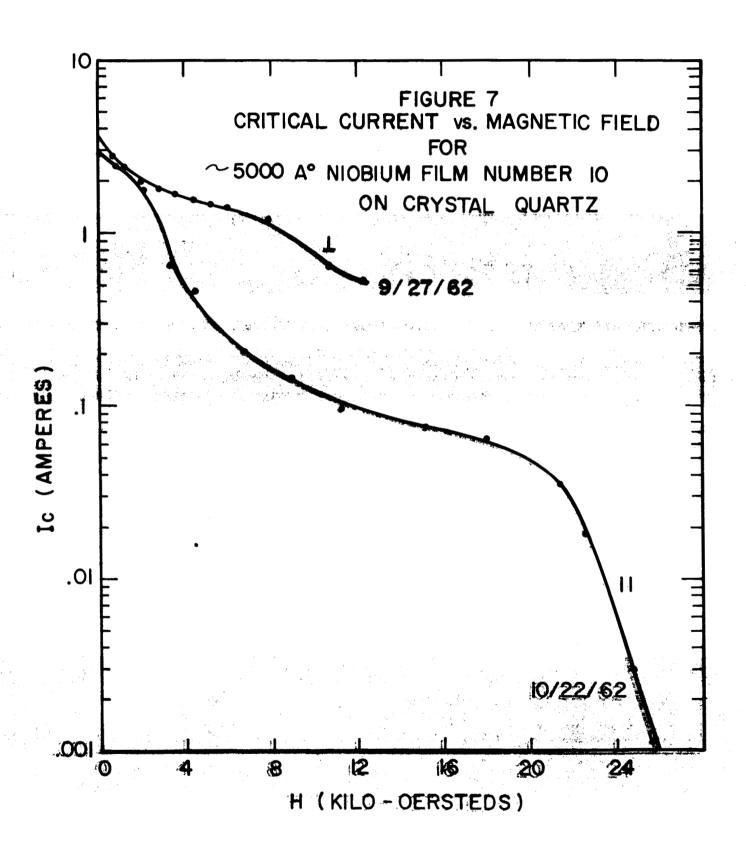
The niobium films obtained appeared shiny, metallic, uniformly reflected visible light, and were extremely adherent to the quartz substrate. The temperature co-efficient of resistance is found to be equal to that given in the Niobium Data Book. The superconducting critical current at 4.2 K vs. external magnet field for several films are shown in figure 5. The estimated thickness is given for each film. The arrow on the curve for film #9 designates the value of current for which the voltage drop across the contacts showed a relatively high power dissipation which could have caused a temperature increase thus limiting the critical current for smaller fields. The current through the copper substrate of film #14 was measured independently and subtracted from the data before plotting.

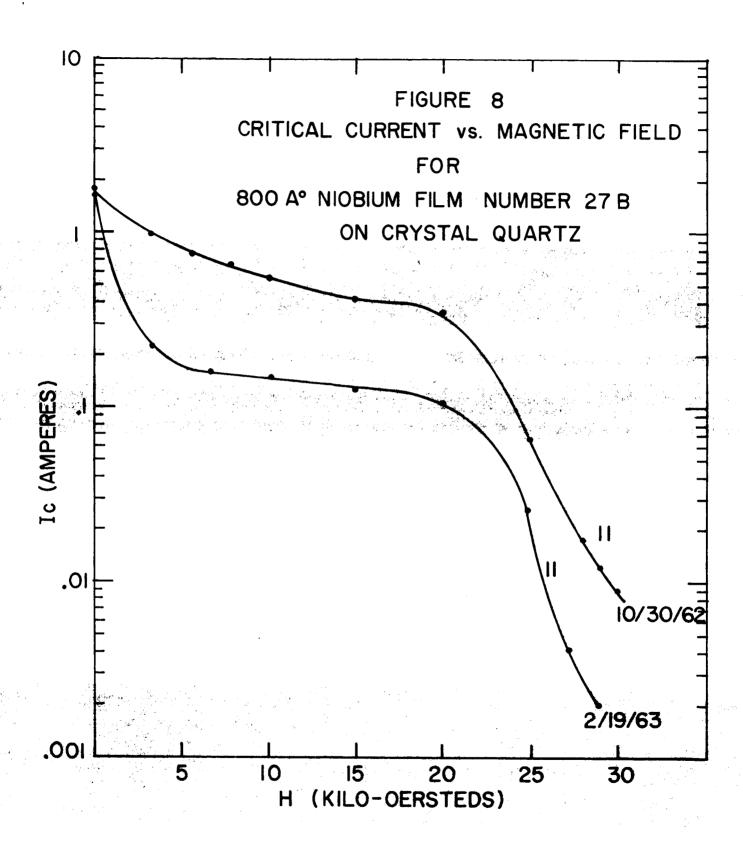
We see that the critical field is much greater than that reported for bulk niobium  $^{8,9}$ . From estimated thickness the critical current at zero magnetic field is found to range from  $5 \times 10^{-5}$  amps/cm<sup>2</sup> to  $5 \times 10^{-6}$  amps/cm<sup>2</sup>. The thickness of one film was measured by electron microscopy of a shadowed replica. We were able to calculate the critical current at zero field to be  $1.6 \times 10^{-6}$  amperes/cm<sup>2</sup>. It should be noted that this film had been estimated to be 260 Angstrom units thick from measurement of its room temperature resistance.

Figures 6, 7, & 8, show data for some niobium films in both transverse and longitudinal fields with some data taken









at later times from the other. Two things are evident. First, there appears to be a definite aging effect which decreases the critical current at non-zero fields but does not greatly affect the zero field critical current. This might be due to the formation of an oxide layer or possibly the slow annealing of strains of a disordered lattice. Since the room temperature resistance of the film and the zero field properties are not affected it is unlikely that a large oxide layer is formed.

Secondly, we see that since the films show similar high field characteristics in both transverse and longitudinal fields, thus we are not observing a simple thin film London type of critical field enhancement, since a transverse field would cause the sample to go into the intermediate state and show much different superconducting characteristics. It is more likely that the high field superconducting characteristics is due to a substructure of the filamentary type as discussed by Goodman and others.

The tin evaporations were carried out in a tantalum boat as discussed earlier. There were several methods attempted in the formation of an Nb Sn film. These are:

- 1) sequential deposition of niobium and tin with subsequent heat treatment in a furnace flushed with purified argon,
- sequential deposition of niobium and tin onto an unheated substrate,

- 3) codeposition of niobium and tin with heat treatment as in (1),
- 4) codeposition of niobium and tin with subsequent heat treatment in another vacuum chamber,
- 5) codeposition of niobium and tin onto a heated substrate and,
- 6) codeposition of niobium and tin with no heat treatment

  except for normal radiant heat from crucible and boat

  plus heat of condensation of the vapors.

The heat treatment in argon is carried out by placing the film in a quartz or vycor tube through which the argon is passed. A thermocouple is placed in a protecting tube next to the sample. The tube is inserted in a Sentry globar furnace which has a zone heated uniformly to  $\pm$  5°C that is 2 inches long. The argon of commercial purity is purified further by passing it through a copper coil cooled in a solid CO<sub>2</sub> - acetone bath and then through a 24 mm diameter vycor tube packed for 14 inches with uranium chips. The tube is heated to 800 C in a tube furnace.

The heat treatment in vacuum is carried out using the heat from a 1-5/8 inch wide resistively heated molybdenum 7 mil thick strip. The strip has a 1-½ inch x ½ inch rectangle cut in it leaving two parallel 1/8 inch wide paths to provide a high temperature zone. A substrate holder of graphite is milled to fit into this space. After placing the substrate in the holder the

heater system is surrounded with a blanket of Fibre Frax (aluminum silicate fibers) allowing the substrate a line of sight view to the vapor source. With this arrangement temperatures in excess of  $1100^{\circ}$ C are attained. The temperature is measured with a thermocouple touching the substrate and covered by the Fibre Frax blanket.

Though no auxiliary means of heating the substrate were employed in methods (2) or (6) above, the temperature of the substrate holder reached 250°C to 300°C during the evaporation. This is to be expected since there is considerable heat radiated from the source of tin and niobium and in addition, there may be substantial heat liberated during the condensation of the vapor on the substrate.

Table II is a list of the experiments made in order to obtain an  $\mbox{Nb}_3\mbox{Sn}$  film. The substrate was polished crystal quartz unless otherwise specified.

The first runs (22-28 in Table II) which were carried out followed the successful method used at NRC for forming Nb<sub>3</sub>Sn by heating of niobium and tin layers in contact. Except in the case of #25 there was no superconductivity measured in the resulting films. #25 was heated for only one minute. X-ray diffraction of #25 shows it to be predominantly NbO<sub>2</sub>. Nb or Nb<sub>3</sub>Sn could be present in an amount too small for X-ray diffraction to detect.

We see that  ${\rm Nb0}_2$  is formed in these experiments. Later experiments have shown that even in the system with purified argon

TABLE II SUMMARY OF Nb<sub>3</sub>Sn EXPERIMENTS

X-ray Structures		!!!	!	$NbO_2$ , $\beta$ -Sn	${ m NbO}_2$	$^{ m Nb}_2{}^{ m Sn}_3$	${ m NbO}_2$	Nb <sub>3</sub> Sn	NbN or NbC	! !	1	none of normal Nb compounds	Nb <sub>3</sub> Sn, Nb	none of normal Nb compounds	$^{\mathrm{Nb}_{2}\mathrm{Sn}_{3}},\mathcal{A}^{-\mathrm{Sn}}$	$^{ m Nb}_2{ m Sn}_3$	Nb, very weak  -Sn
Super- conductive Properties		none	insulator	auou	slight	none	insulator	none	none	none	none	none	yes	<b>sl</b> ight	none	none	yes
Maximum Treatment Temperature		1130	820	086	820	830	086	280	006	026	026	870	<250	820	240	250-300	250
Time		7 min	7 min	7 min	1 min	l min	5 min	1	10 sec	10 sec	20 sec	10 sec	10 sec	8 min	15 sec	8 sec	11 sec
Treatment		argon	argon	argon	argon	argon	vacuum 5 3 x 10 torr	none	vacuum 5 torr	vacuum 5 torr	vacuum 5 torr	vacuum_5 l x 10 <sup>-5</sup> torr	vacuum_5 torr	vacuum 7 torr	vacuum 5 torr	vacuum_5 torr	vacuum_5 1 x 10 <sup>-5</sup> torr
Method of Deposition	172 3 QZ	sequential	sequential	sequential	sequential	simultaneous	simultaneous	simultaneous	simultaneous	simultaneous	simultaneous	simultaneous	simultaneous	sequentia1	simultaneous	simultaneous	simultaneous
Film Name of	Number	22	23	24	25	28	29-1	29-2	32	33	34	36	36G	37-2	38	49	65

In the simultaneous deposition runs the defocusing of the beam by the current flow through the tin boat caused thinner films than expected. Note:

mentioned earlier contamination occurred unless the quartz tube in which treatment is carried out is first heated to about 1000°C and flushed with purified argon until the sample is introduced. This was not carried out in the samples listed in Table II.

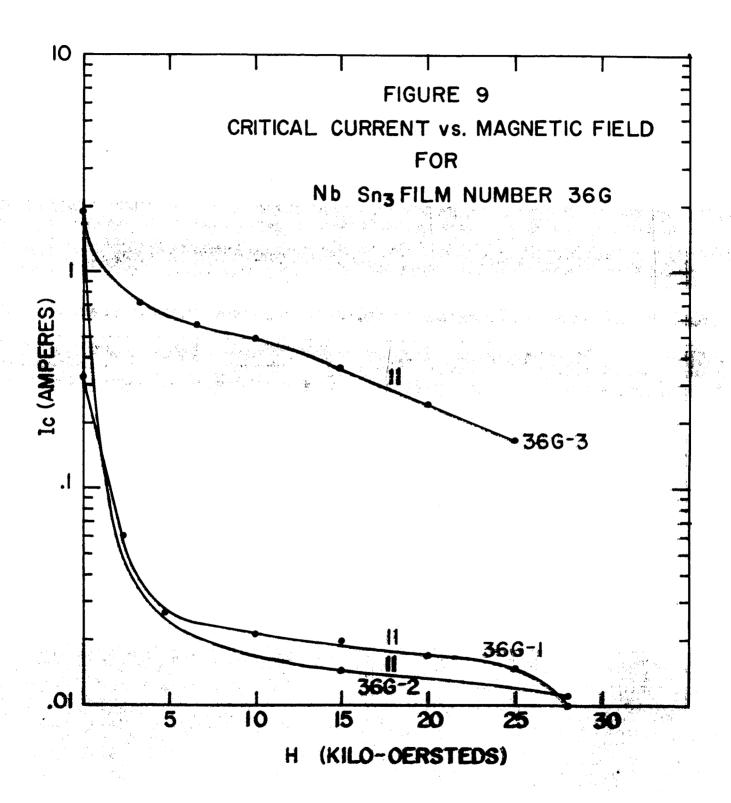
Another possibility for the oxide formation would be reduction of the SiO<sub>2</sub> substrate in the manner Nb+SiO<sub>2</sub> NbO<sub>2</sub>+Si or Nb+2SiO<sub>2</sub> NbO<sub>2</sub> + 2SiO. However, from tabulated values of free energy change for such reactions we find that this is unlikely. X-ray evidence shows that reduction of the quartz is unlikely since NbO<sub>2</sub> is detected only for the cases of treatment in the argon system or the one case (#29-1) of treatment in vacuum. In this latter case a leaking 0-ring seal near the heated sample had caused degradation of vacuum conditions. Experiments performed in high vacuum produced films with no detectable NbO<sub>2</sub> formation.

Simultaneous evaporations of the Nb and Sn were carried out onto substrates heated to 850 - 970 C in runs 32 - 36.

No superconductivity was found in these films and one film #32 investigated by X-ray diffraction gave inconclusive identification of NbC or NbN in the films. Film #36 showed a fairly strong diffraction pattern but could not be identified as any of the normal compounds of niobium or tin.

A check of the films deposited along with the samples treated and retained for comparison and analysis showed X-ray evidence of Nb<sub>3</sub>Sn and Nb<sub>2</sub>Sn<sub>3</sub>formation. The latter compound has been shown by Reed and Gatos<sup>13</sup> and by Wyman, etal<sup>14</sup> to be a low temperature non-superconducting phase for the Nb-Sn system. One of the Nb<sub>3</sub>Sn films (#29-2) showed no superconducting properties at 4.2°K but the other (#36-G) did exhibit superconductivity. Two samples of 36-G were cut from one end of a 3 inch x 1 inch microscope slide that had been coated and a third from near the center of the slide. The critical current vs. external magnetic field for these samples is shown in Figure 9.

Since it appears that much lower substrate temperatures are desirable than that used in the normal process of formation of Nb<sub>3</sub>Sn, <sup>15, 16, & 17</sup> therefore deposition was carried out at 540°C for film #38. X-ray diffraction showed formation of the compound Nb<sub>2</sub>Sn<sub>3</sub> and also that there was an excess of Sn. Since film #36-G proved to contain Nb<sub>3</sub>Sn plus excess Nb we were led to the idea that by proper control of the rates of evaporation of niobium and tin, the correct ratio of atoms can be condensed in order to obtain the desired stoichiometric compound of niobium and tin. It is felt that this is more important than substrate temperature in the determination of whether Nb<sub>3</sub>Sn or Nb<sub>2</sub>Sn<sub>3</sub> is formed.



The work of Gunther on InAs and InSb and that of Fowler,

19
Koller and Schrank on Cs<sub>3</sub>Sb has shown that by co-depositing
the vapors of the elements a compound can be formed with
substrate temperatures less than required for formation in the
corresponding solid or liquid diffusion processes.

The power input to the niobium source is kept constant with relative ease by varying cathode emission. The power input to the source of tin is less easily controlled. radiative heating, electron bombardment heating, and direct resistance heating were investigated. The temperature required for indirect heating and the problems associated with electrical discharge in the presence of vaporizing tin have led us to conclude that direct resistive heating utilizing a rather large reservoir for the tin is preferable. Two codepositions of Nb and Sn, #49, #65, were made using such a tin source. These proved to show  $\mathrm{Nb}_2\mathrm{Sn}_3$  formation in one case and no compound In this latter case very little tin formation in the other case. was found to be present thus showing further development work on a satisfactory source for tin vapor is required. One problem that showed itself in the simultaneous deposition runs is the effect of the current through the tin boat on the electron beam. beam is generally focused prior to a run and thus when the 100 - 300 amperes required for heating the tin source is passed through the boat the resulting magnetic field causes deflection of The leads to the tin boat were arranged so as to

minimize this effect for experiment #65. This may explain the reason for the large ratio of Nb to Sn present in the resulting film.

#### SUMMARY

As a preliminary step in this investigation, several niobium films were prepared. They showed superconducting properties in fields as high as 30,000 oersteds. The critical current densities at zero external magnetic fields for these films were in the order of 10 6 amperes per square centimeter.

It was shown that Nb<sub>3</sub>Sn coatings may be prepared by codeposition of Nb and Sn vapors onto a substrate heated to temperatures less than 300°C. Evidence suggests that control of the vapor pressure is important in order to attain the correct stoichiometric ratio of molecules to form the desired compound. Future work should attempt to improve the temperature control of the vapor sources.

Testing of the superconductive properties of films produced was carried out in external magnetic fields of 30,000 oersteds where appropriate.

Although the investigation has not reached the point whereby coatings of the desired current carrying capability may be prepared it is felt that with continued work that goal could be reached and a coating applied to a cylindrical substrate.

#### ACKNOWLEDGEMENTS

The author wishes to acknowledge discussion with Dr. Alvin F. Hildebrandt who suggested the problem and the general method to follow. He would also like to acknowledge the help of Mr. Frank Pink in performing X-ray diffraction analysis and that of Mr. John Webster in preparing the films.

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